



ACSSI2012

ACSSI 2012

The 13th Asian Conference on Solid State Ionics
IONICS for sustainable world

ABSTRACTS



17th to 20th July, 2012 Sendai, Japan



ACSSI 2012

The 13th Asian Conference on Solid State Ionics

17th to 20th July, 2012

Katahira Sakura Hall, Tohoku University, Sendai, Japan

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Prof. Junichiro Mizusaki

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Editors

Prof. B.V.R. Chowdari

National University of Singapore, Singapore

Prof. Junichi Kawamura

IMRAM, Tohoku University

Prof. Junichiro Mizusaki

IMRAM, Tohoku University

Prof. Koji Amezawa

IMRAM, Tohoku University

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B. V. R. Chowdari

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¹ ICMCB-CNRS, Université de Bordeaux, 87, av. Dr. Schweitzer, 33608 Pessac, France

² CEA-Grenoble, DRT-LITEN, 17, rue des Martyrs, 38054 Grenoble, France

³ Université de Bordeaux, CREMEM, 33405 Talence, France

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¹ WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

² Toyota Motor Corporation, Shizuoka 410-1193, Japan

³ Graduate School of Frontier Sciences, The University of Tokyo, Chiba 277-8561, Japan

⁴ Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

⁵ Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan

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¹ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China

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¹ Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

² Department of Physics, Faculty of Science and Technology, State Islamic University (UIN) Alauddin, Makassar, Indonesia

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Mohan L. Verma¹, B. Keshav Rao¹, Nirbhay Singh² and Homendra Sahu¹

¹ Condensed Matter Physics Research Laboratory, Department of Applied Physics and Material Science, Faculty of Engineering and Technology, Shri Shankaracharya Technical Campus - Junwani, Bilai (Chhattisgarh) INDIA

² Department of Applied Physics, Shri Shankaracharya Institute of Engineering & Technology - Khapri, Durg (Chhattisgarh) INDIA

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Department of Applied Physics, Visvesvaraya National Institute of Technology, Nagpur (India).

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A THEORETICAL ANALYSIS OF PHYSICAL PROPERTIES OF AQUEOUS TREHALOSE WITH BORAX

SAHARA

*Department of Physics, Graduate School of Science and Technology, Kumamoto University,
Kurokami 2-39-1, Kumamoto, 860-8555, Japan.
Department of Physics, Faculty of Science and Technology,
State Islamic University (UIN) Alauddin, Makassar, Indonesia.*

MASARU ANIYA

*Department of Physics, Graduate School of Science and Technology, Kumamoto University,
Kurokami 2-39-1, Kumamoto, 860-8555, Japan.*

The temperature and composition dependence of the viscosity of aqueous trehalose and aqueous trehalose-borax mixtures has been investigated by means of the Bond Strength-Coordination Number Fluctuation (BSCNF) model. The result indicates that the variation in the fragility of the system is very small in the composition range analyzed. The values of the materials parameters determined are consistent with those of the trehalose-water-lithium iodide system which were analyzed in a previous study. Based on the analysis of the obtained parameters of the BSCNF model, the physical interpretation of the WLF parameters reported in a previous study is reconfirmed.

1. Introduction

Trehalose is well-known for its ability to preserve life in cells, organisms, and biomolecules under conditions of low temperatures. Therefore, the effect of salt and other chemicals in trehalose solutions provides an interesting field of study from both, academic and applied science point of views. Experimental studies have shown that NaCl in aqueous trehalose mixtures is fully dissociated close to the glass transition temperature [1]. With the objective to gain further understanding on the properties of aqueous trehalose doped with salt and other chemicals, we have studied the viscosity behavior of these systems by using the Bond Strength-Coordination Number Fluctuation (BSCNF) model.

In a previous study, we have analyzed the temperature dependence of the viscosity in disaccharide solutions such as trehalose, maltose and sucrose [2]. The result revealed that these systems are fragile system. We have also analyzed the viscosity behavior of trehalose-water-lithium iodide system. This system is interesting from the point of view of ionic conduction, because the ionic conductivity of the system can be changed largely by controlling the chemical composition of the system [3, 4]. That is, it is expected that the optimization of the ionic conductivity could be searched by studying the viscosity-conductivity relation.

Recently, a comparative study between different theoretical models that describe the temperature dependence of the viscosity has been done [5]. The result indicated that the parameters of the BSCNF model, the VFT (Vogel-Fulcher-Tamman) equation and the WLF (Williams-Landel-Ferry) equation can be interrelated. This means that the parameters evaluated through VFT or WLF equations can be interpreted in terms of the BSCNF model which has clear physical meanings. In the present work, with the objective to gain further understanding on the physical properties of trehalose system, the BSCNF model has been applied to investigate the temperature dependence of the viscosity of aqueous trehalose and aqueous trehalose-borax mixtures.

2. Model for the viscosity

2.1. The BSCNF model

In the BSCNF model, the melt is considered to be formed by an agglomeration of structural units. When the temperature of the system is lowered, the viscosity of the melt increases due to the increase of the connectivity between the structural units and the spatial distribution of the structural unit is frozen at the glass transition temperature T_g . According to the model, the viscous flow occurs when the structural units move from one position to another by twisting or breaking the bonds connecting them. Each structural unit is bound to other structural units by certain bond strength [6].

Based on the above considerations, the temperature dependence of the viscosity has been written as

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx + Cx^2 \left\{ \left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2} \ln(1-B) \right] \frac{(1-B)}{C} - 1 \right\}}{1 - Bx^2} - \frac{1}{2} \ln(1 - Bx^2), \quad (1)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2}, \quad C = \frac{E_0 Z_0}{RT_g}, \quad \text{and} \quad x = \frac{T_g}{T}. \quad (2)$$

In Eq. (1), η_0 and η_{T_g} denote the viscosities at the high temperature limit and at the glass transition temperature, respectively. For their values we adopted the usual values $\eta_0 = 10^{-5}$ Pa·s and $\eta_{T_g} = 10^{12}$ Pa·s [7]. C contains information about the total bond strength of the structural unit and B gives its fluctuation. E_0 and Z_0 are the average values of the binding energy and coordination number of the structural units, respectively. ΔE and ΔZ are their fluctuations. R is the gas constant.

According to the BSCNF model, the fragility index m is written in terms of the parameters B and C as [6, 8]

$$m = \frac{1}{\ln(10)} \left\{ \frac{B - C + 2 \left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2} \ln(1-B) \right]}{1-B} \right\}. \quad (3)$$

From Eq. (3), we can learn that a high value of the total bond strength of the structural unit C and a low value of its fluctuation B corresponds to a less fragile system [9].

It has been shown that the quantities B and C are related by the following relation [8]

$$C = \frac{2x(1-B)}{2x + \sqrt{B(1+x^2)}} \left\{ \ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2} \ln(1-B) \right\}, \quad (4)$$

where,

$$x = \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0}. \quad (5)$$

When $X = 1$, that is, when the ratio of the normalized bond strength fluctuation to the normalized coordination number fluctuation equals unity, the above Eq. (4) reproduces exactly the well known Vogel-Fulcher-Tammann behavior by choosing appropriately the values of B and C [8].

2.2. The WLF Equation

The WLF equation has been used widely to describe the temperature dependence of the viscosity and relaxation time in polymeric systems. It is an empirical equation and is given by

$$\log a_T = \log \left(\frac{\eta}{\eta_{T_g}} \right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}, \quad (6)$$

where a_T is called shift factor. η is the viscosity at temperature T and η_{T_g} is the viscosity at some reference temperature. In the above expression, we have used the glass transition temperature T_g as the reference temperature. C_1 and C_2 are constants [10]. It has been reported that the values of C_1 and C_2 are 17.4 and 51.6 K respectively, for many materials [10, 11]. In terms of the WLF parameters, the fragility is given by [11]

$$F = 1 - \frac{C_2}{T_g}. \quad (7)$$

3. Results and Discussion

The BSCNF model and the WLF equation have been applied for the investigation of the temperature dependence of the viscosity of aqueous trehalose and aqueous trehalose-borax systems. In our study, the experimental data of the viscosity of aqueous trehalose-borax at nominal trehalose mole fraction, X_T , of 0.075 and boron mole fraction, X_B between zero and 0.1515 are used as test materials [12]. From a fitting of Eq. (1) to the experimental data, we have determined the values of the parameters B and C corresponding to BSCNF model. Concerning the value of the fragility index m and F , we have determined them from Eq. (3) and Eq. (7), respectively. The results of the analysis are summarized in Table. 1.

Table 1. Numerical values of the parameters of BSCNF model (B , C), and the WLF (C_1 , C_2) equation [12]. The experimental values of the glass transition temperature T_g , and the fragility index F and m for various trehalose-borax solutions are also given.

Solutions	B	C	C_1	C_2 (K)	T_g (K)	F	m
X_T : 0.0316, X_B : 0	0.772	9.62	15.26	19.40	159.7	0.88	129.45
X_T : 0.0465, X_B : 0	0.774	9.53	15.45	23.99	174.0	0.86	130.76
X_T : 0.0601, X_B : 0	0.775	9.48	15.37	24.80	185.5	0.87	131.44
X_T : 0.0749, X_B : 0	0.780	9.25	15.48	26.26	199.1	0.87	134.82
X_T : 0.1339, X_B : 0	0.789	8.85	12.08	11.85	229.6	0.95	141.34
X_T : 0.0749, X_B : 0.0224	0.793	9.55	15.27	25.33	204.5	0.88	142.58

X_T : 0.0749, X_B : 0.0597	0.792	9.96	14.87	24.10	213.3	0.89	141.04
X_T : 0.0747, X_B : 0.0748	0.789	10.61	14.91	26.19	216.9	0.88	137.72
X_T : 0.0750, X_B : 0.1123	0.790	10.03	14.70	24.93	224.7	0.89	139.57
X_T : 0.0751, X_B : 0.1515	0.791	9.97	14.15	22.01	233.8	0.91	140.36

The relation between the parameters B and C of the BSCNF model obtained for different materials is shown in Fig. 1. The results for aqueous trehalose and aqueous trehalose-borax systems are shown in colored symbols. Due to the small variation in the composition range analyzed, the relation seems almost overlapping. In any way, for further understanding of the effect of addition of trehalose or borax in the solutions, the composition range should be extended. This is important, because the ionic conductivity of the trehalose system can be changed largely by controlling the chemical composition of the system [3, 4].

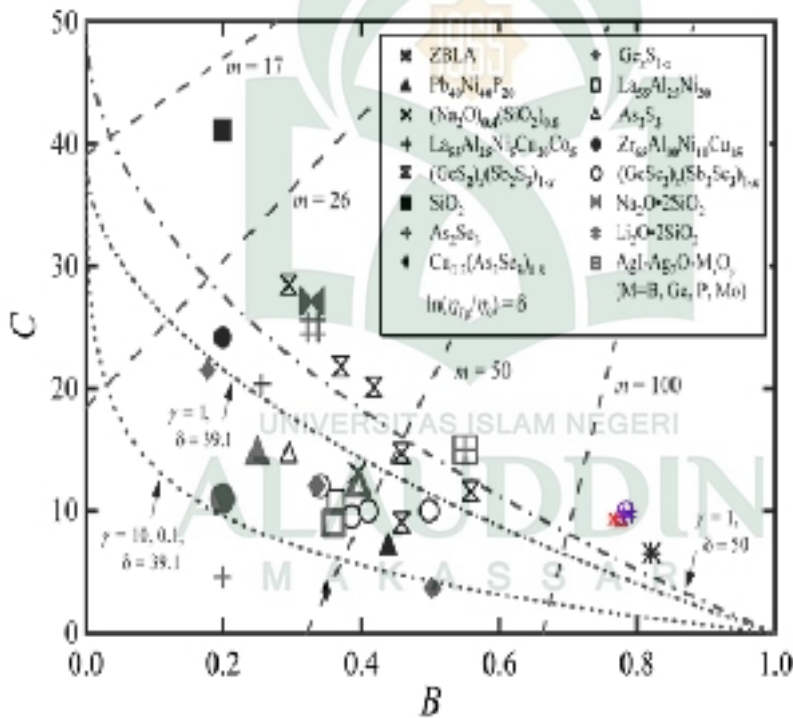


Figure 1. Relationship between the values of parameters B and C determined for different materials [13]. Red and violet symbols represent the parameters of aqueous trehalose and aqueous trehalose-borax systems, respectively.

Although the effect of trehalose concentration in the solutions fragility is not so clear in Fig. 1, the result provides an estimation for the values of B and C , that is $B \cong 0.78$ and $C \cong 9$. For the trehalose-borax system, similar values are obtained. These values are close to the values of parameters determined in trehalose-water-lithium iodide system by making use conductivity data, $B \cong 0.3 - 0.7$ and $C \cong 5 - 18$. [3]. As discussed elsewhere, the value of C and B are related respectively with the total bond strength and its fluctuation of the structural units that form the melt. From Fig. 1 we can see also that the systems studied exhibit value of u close to the ZBLA

system. Analysis based on the BSCNF model indicates that the relation between B and C depends on the value of u [13]. The figure indicates that the systems in consideration is described by Eq. (4) by adopting the value of $u = \ln (T_g/0) = 80$.

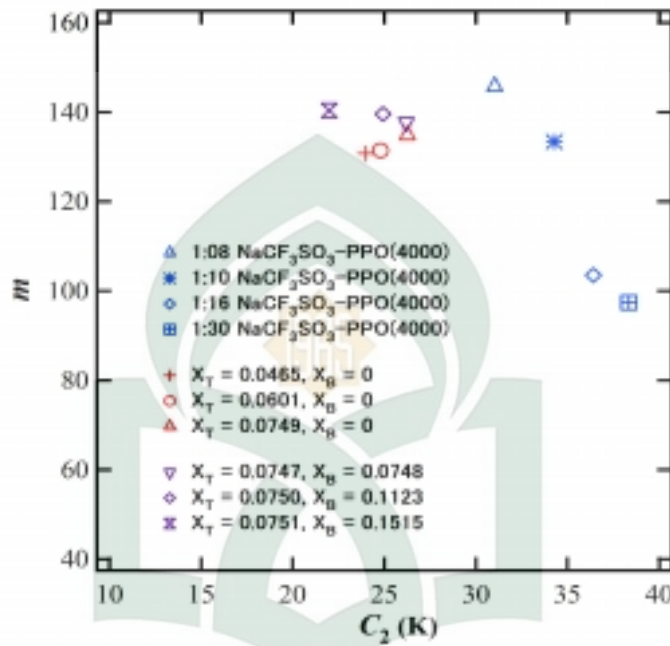


Figure 2. Relationship between the fragility calculated from the BSCNF model, Eq. (3) and the value of the parameter C_2 in the WLF equation.

In a previous study we have suggested that the BSCNF model could provide a physical interpretation to the empirical parameter C_2 of the WLF equation. Here, such a suggestion is considered for the case of aqueous trehalose-borax system. A comparison between C_2 and the fragility index described by the BSCNF model is shown in Fig. 2. For the case of polymer systems, it has been shown that m decreases with the increase of C_2 [5]. For the case of aqueous trehalose-borax system no clear trend is discernible. It could be caused by the limited composition and temperature ranges of the experimental data used in the analysis. In Fig. 3, a comparison between the fragility index described by the BSCNF model and the values of fragility calculated from Eq. (7) is shown. We can see that the two sets of data vary systematically. In the figure, the result of a previous study performed for polymeric systems is also shown. For this system, a clear linear relationship between m and F are discernible.

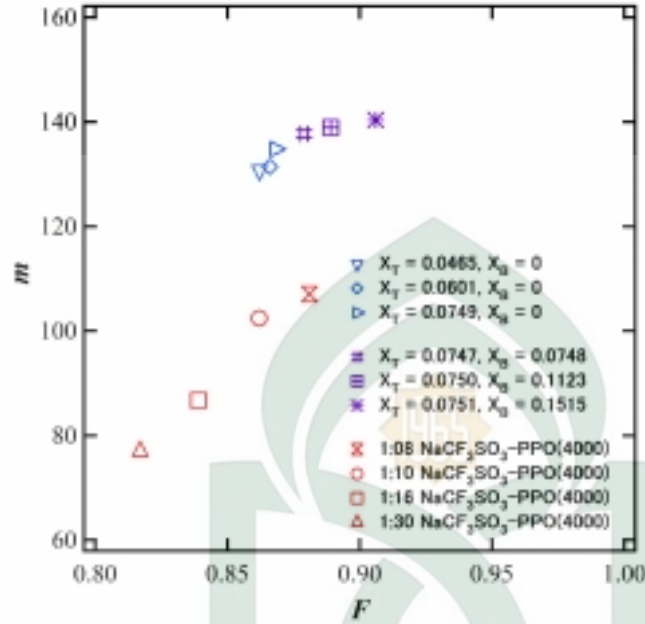


Figure. 3 Relationship between the fragility index calculated by the BSCNF model, Eq. (3) and the fragility given by Eq. (7).

The temperature dependence of the viscosity for aqueous trehalose and aqueous trehalose-borax systems calculated through Eq. (1) is shown in Fig. 4. It is noted that the theoretical curve fits well the experimental data in the intermediate temperature region. However, deviation becomes apparent at low temperature. From the figure, it is noted that the system in consideration is relatively fragile, as expected from the values of B and C shown in Fig. 1.

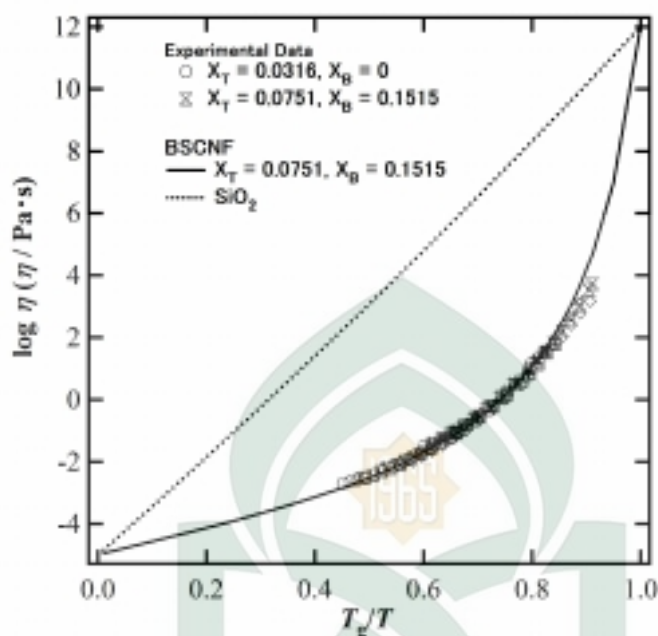


Figure. 4. Temperature dependence of the viscosity for aqueous trehalose and trehalose-borax systems obtained from Eq. (1). The behavior of SiO_2 is also shown for comparison

4. Conclusion

The Bond Strength-Coordination Number Fluctuation (BSCNF) model and the WLF equation have been used to study the viscosity behavior of aqueous trehalose and trehalose-borax mixtures. The result indicates that both models describe well the temperature dependence of the viscosity reported experimentally. The analysis based on the BSCNF model suggests that the variation in the fragility is very small in the composition range analyzed. From the comparison of these models, it was shown that the BSCNF model could provide a physical interpretation to the empirical parameters used in the WLF equation.

Acknowledgments

Sahara acknowledges for the Monbukagakusho Scholarship.

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